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(54) FLUORESCENT INK COMPOSITION AND FLUORESCENT MARK FORMED OF THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a fluorescent ink composition not blotting and improved in dispersion stability, light fastness, heat resistance and water resistance by mixing a fluorescent dye with specified fine organic particles.
SOLUTION: Fine organic particles having a glass transition temperature of 30° C or above and a particle diameter of 30nm or above are mixed with 0.001-15wt.% organic dye and or white optical brightener each of which fluoresces in an infrared wavelength region of 700nm or longer to obtain a fluorescent ink composition used for an ink jet printer and having a viscosity (mPa.s)/nozzle aperture (,,m) ratio of 0.01-1, a Reynolds number of 10.5-2,100, a Weber number of 38.2-3,360 and a viscosity (mPa～s)/surface tension ratio of 0.03-1.0.

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[Claim(s)]

[Claim 1] A fluorescence ink constituent which particle diameter shows fluorescence in a light field above 30 degrees C, glass transition temperature including an organic particle 30nm or more [Claim 2] An infrared fluorescence ink constituent which particle diameter absorbs infrared light with a wavelength of 700nm or more, glass transition temperature including an organic particle 30nm or more, and shows luminescence to an infrared region above 30 degrees C [Claim 3] A fluorescence ink constituent characterized by a part or all of an organic particle according to claim 1 being an empty capsid [Claim 4] An infrared fluorescence ink constituent characterized by a part or all of an organic particle according to claim 2 being an empty capsid [Claim 5] Claim 1 whose relation between viscosity (mPa-s)/nozzle diameter (micrometer) is the fluorescence ink constituent for ink jet printers of 0.01-1, claim 2, a fluorescence ink constituent according to claim 3 or 4 [Claim 6] Claim 1 whose Reynolds number is the fluorescence ink constituent for ink jet printers of 10.5-2100, claim 2, claim 3, a fluorescence ink constituent according to claim 4 or 5 [Claim 7] Claim 1 whose Weber number is the fluorescence ink constituent for ink jet printers of 38.2-3360, claim 2, claim 3, claim 4, a fluorescence ink constituent according to claim 5 or 6 [Claim 8] Claim 1 whose relation between viscosity (mPa-s)/surface tension is the fluorescence ink constituent for ink jet printers of 0.03-1.0, claim 2, claim 3, claim 4, claim 5, a fluorescence ink constituent according to claim 6 or 7 [Claim 9] A fluorescence mark whose particle diameter shows fluorescence in a light field above 30 degrees C, glass transition temperature including an organic particle 30nm or more [Claim 10] A fluorescence mark characterized by a part or all of an organic particle according to claim 9 being an empty capsid [Claim 11] An infrared fluorescence mark which particle diameter absorbs infrared light with a wavelength of 700nm or more, glass transition temperature including an organic particle 30nm or more, and shows luminescence to an infrared region above 30 degrees C [Claim 12] An infrared fluorescence mark characterized by a part or all of an organic particle according to claim 11 being an empty capsid [Claim 13] An infrared fluorescence mark according to claim 11 or 12 10 - 90% of

whose build up time of the luminescence maximum output when irradiating infrared light at an infrared fluorescence mark is less than 10microsec

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] About the fluorescence mark formed with a fluorescence ink constituent and this fluorescence ink constituent, a blot does not arise, and this invention does not have in more detail, the blot formed with the fluorescence ink constituent excellent in distributed stability, lightfastness, thermal resistance, and a water resisting property, and this fluorescence ink constituent, and relates to the high-concentration fluorescence mark excellent in lightfastness, thermal resistance, and a water resisting property.
[0002]
[Description of the Prior Art] In recent years, information, such as a manufacturer, a trade name, etc. about an article, is displayed by a bar code etc., and using the striped pattern for the sales total of goods, analysis of a negotiation, etc. as reading by the optical detecting method is performed. This kind of bar code is printed using an ink jet printer etc., and is usually suitable for a classification of the goods in the dealer treating a variety of goods etc., and discernment. For this reason, recently, it is used for the mail which applies the system which there are [many goods using this bar code system are not only seen, but] some which applied this system to file management etc., for example, distributes an article by division by code management.
[0003] however, as a method of printing a bar code, conventionally Since the method of printing a black bar code to a white ground is adopted and this method uses the difference of the reflection factor of a white ground and black figures, Since it has the defect that a readout becomes difficult extremely and the reflected light of a visible region is further used inevitably by this method when dirt arises on articles, the appearance of an article may be spoiled.
[0004] For this reason, as an amelioration type of such a monochrome bar code, it excites by ultraviolet radiation, and the fluorescence mark which emits light in the light is used, or it excites by infrared light, and the infrared fluorescence bar code (****** 6-500590) which emits light in infrared light is proposed.
[0005]
[Problem(s) to be Solved by the Invention] However, since the fluorescent substance which excites by ultraviolet radiation and emits light in the light is what is seen intrinsically in a visible region, it it not only spoils the appearance of an article, but has the problem that reading becomes difficult with the dirt on a mark etc., like

monochrome bar code.

[0006] Moreover, although it is possible for it not to be influenced so much by the dirt on a mark, either, but to detect a mark, without spoiling the appearance of an article by existence of a bar code since it does not have luminescence by the light when the infrared fluorescent substance which excites by infrared light and emits light in infrared light is used Since these infrared fluorescent substances become the wavelength of an infrared region from the infrared fluorescent dye which absorbs and emits light, When a marked object is what is easy to absorb ink like Japanese paper, and this color is ink-ized and it prints with an ink jet printer etc., a blot of the ink called a feathering phenomenon may occur, it may read by this, and a rate may fall and misoperate. Furthermore, although it tends to carry out densification of the record of a bar code, since the gap of a bar code becomes narrow in this case, this phenomenon serves as a fatal defect and has a problem practically. Moreover, the organic dye which that to which a marked object absorbs infrared light, for example, read when black, becomes difficult, and they use for this ink further since the ink of these former has the property to dye the marked object which is the property of color original has lightfastness and a bad water resisting property, and has a problem of it becoming impossible to decode the mark in which it was formed. moreover, the example using the inorganic compound which contains neodymium, an yttrium, etc. as an infrared fluorescent substance -- there is it (the United States Patent official report No. 4202491, JP,54-22326,B, JP,53-9607,A, etc.) -- since these inorganic fluorescent substances have the slow rate of rise which emits light in infrared light, when reading the mark of a bar code etc. at high speed, the adjoining mark and output lap and they have the problem that distinction of a mark cannot be performed.

[0007] When this invention was not made as a result of examining many things in view of this actual condition, a blot does not produce it, but the fluorescence ink constituent excellent in distributed stability, lightfastness, thermal resistance, and a water resisting property is offered and it forms a fluorescence mark using print devices, such as an ink jet printer, there is no blot and the high-concentration fluorescence mark excellent in lightfastness, thermal resistance, and a water resisting property is obtained. Moreover, the infrared fluorescence mark suitable for the densification of a bar code is obtained, without being able to perform good reading and limiting a marked object, even when an infrared fluorescence mark is prepared on the marked object which has infrared absorption. Furthermore, there is no sedimentation, conservation stability is good, and when there is no condensation of ink and desiccation solidification is carried out, it is going to offer the ink constituent for ink jet printers excellent in redispersible which is satisfactory practically.

[0008]

[Means for Solving the Problem] As for a fluorescence ink constituent of this invention, particle diameter shows luminescence to an infrared region, while glass transition temperature is 30 degrees C or more, an organic particle, a part, or all 30nm or more shows fluorescence in a light field including an organic particle whose particle diameter is an empty capsid, and glass transition temperature is 30 degrees C or more and an organic particle, a part, or all 30nm or more absorbs infrared light with a wavelength of 700nm or more including an organic particle which is an empty capsid.

[0009] Moreover, relation between viscosity (mPa-s)/nozzle diameter (micrometer) is 0.01-1, and the Reynolds number is [10.5-2100, and a Weber number] 38.2-3360, and he is trying, as for a fluorescence ink constituent for ink jet printers of this invention, for relation between viscosity (mPa-s)/surface tension in 0.03-1.0 to become.

[0010] Furthermore, glass transition temperature of a fluorescence mark of this invention is 30 degrees C or more. Particle diameter shows fluorescence in a light field including an organic particle whose organic particle, part, or all 30nm or more is an empty capsid. Glass transition temperature above 30 degrees C Particle diameter contains an organic particle whose organic particle, part, or all 30nm or more is an empty capsid. While absorbing infrared light with a wavelength of 700nm or more, luminescence is shown in an infrared region, and he is trying for 10 - 90% of build up time of the luminescence maximum output when irradiating infrared light further to become less than 10microsec.

[0011]

[Embodiment of the Invention] As for the organic particle contained in the fluorescence ink constituent of this invention, it is desirable that glass transition temperature is 30 degrees C or more, and particle diameter is a thing 30nm or more, and stability with a glass transition temperature good [an organic particle 30 degrees C or more] also when ink is warmed and it is used to near 40 degree C in order the stability of a print is good when printed with an ink jet printer, and to bring drying [of ink] forward like recently, and the stability over heat is searched for is acquired.

[0012] Especially, within the system of a print device, when the temperature of ink may rise to near 30 degree C and ink is saved especially summer, an organic particle originates in the property of the raw material, comes to show adhesiveness, and produces condensation of ink. Moreover, although an image may imprint to the contactant when an image is formed in paper since the adhesiveness of an organic particle is seen even after it forms an image for example, the ink which is excellent in the conservation stability which is not imprinted after image formation and thermal resistance is obtained, without causing viscosity lifting, even if ink serves as an elevated

temperature if the glass transition temperature of an organic particle is 30 degrees C or more. In addition, although it will not be restricted especially if it is 30 degrees C or more since the above-mentioned property will fully discover it, if the glass transition temperature of an organic particle is 30 degrees C or more, 30 degrees C or more 400 degrees C or less are desirable on the construction material of an organic particle, and 30 degrees C or more 350 degrees C or less are more desirable.

[0013] Moreover, sufficient printing concentration is obtained, and if the organic particle of this invention is set to 30nm or more, since it will become possible [connoting coloring matter in an organic particle], it can control a blot of ink good further, while distributed stability equivalent to a color will be acquired, if particle diameter is 30nm or more. Moreover, since redispersible [of ink] is required when using for ink jet printers while control of the particle diameter in manufacture is easy, when it is 30nm or more, it is required not to carry out film formation, but in the ink using the organic particle of this invention, since wettability with a solvent is good, suitable ink can be obtained also at this point.

[0014] In addition, although it becomes [an image] clearer and is more desirable as particle diameter is large since concealment nature of an organic particle improves so that particle diameter becomes large, 30nm or more 2 micrometers or less are desirable from the point of versatility, and 30nm or more 0.8 micrometers or less are more desirable. As mentioned above, an organic particle is 30nm or more, and when it is 30 degrees C or more, as for the ink constituent of this invention, the thermal stability of ink and redispersible are good, and it can obtain an image without imprint nature.

[0015] Moreover, when using these organic particles, it is more desirable to use an empty capsid also in an organic particle, and the organic particle whose part is an empty capsid is also used preferably. Since such an empty capsid has connoted the solvent in a particle, even when specific gravity does not become large even if particle diameter became large but ink concentration is made high, it can obtain ink excellent in redispersible, without ink carrying out film formation. Moreover, since a refractive index when an empty capsid irradiates light after image formation is different from a particle front face inside, it is desirable also from the point which can improve concealment nature more.

[0016] If particle diameter uses the organic particle whose organic particle, part, or all 30nm or more such a glass transition temperature is an empty capsid above 30 degrees C with fluorescent dye and/or a white fluorescent brightener Above 30 degrees C, glass transition temperature contains [particle diameter] the organic particle whose organic particle, part, or all 30nm or more is an empty capsid. The ink constituent in which fluorescence is shown in a light field is obtained, while excelling in thermal resistance

and distributed stability, a blot does not arise, but the fluorescence ink constituent excellent in lightfastness and a water resisting property is obtained.

[0017] Glass transition temperature above 30 degrees C to moreover, the organic particle whose organic particle, part, or all 30nm or more is an empty capsid [particle diameter] If fluorescent dye and/or a white fluorescent brightener are processed by the massive resin grinding method, the emulsion-polymerization method, the resin depositing method, etc. The colored fluorescent dye which separated is incorporated in the organic particle an organic particle, a part, or whose all is an empty capsid, and impregnation association is firmly carried out. The fluorescence organic pigment which maintained the property of fluorescent dye and/or a white fluorescent brightener as it was is obtained, such a fluorescence organic pigment is used and a fluorescence ink constituent is obtained. Effect of the substrate at the time of printing can be made hard for the fluorescence ink constituent which used such a fluorescence organic pigment to have a property as a pigment, for a blot not to produce it, even if it uses it unlike fluorescent dye, when forming a mark in paper etc., but to excel in distributed stability, lightfastness, a water resisting property, and coloring nature, to be able to give concealment nature, since it is a pigment further, and to be influenced.

[0018] The massive resin grinding method carries out melting mixing of fluorescent dye and/or the white fluorescent brightener here with the organic particle an organic particle, a part, or whose all is an empty capsid. It is the method of grinding the solid obtained after cooling. An emulsion-polymerization method It is the method of carrying out adsorption dyeing of aforementioned fluorescent dye and/or an aforementioned white fluorescent brightener at the suspension of the organic particle whose said organic particle, part, or all that was obtained by carrying out an emulsion polymerization is an empty capsid. The resin depositing method makes the aqueous solution of a metal salt add and react to the aqueous solution which dissolved an organic particle and aforementioned fluorescent dye, and/or an aforementioned white fluorescent brightener. Liquid is made into acidity if needed, and the organic particle whose organic particle, part, or all that is dissolved is an empty capsid is deposited as a metal salt, with fluorescent dye and/or a white fluorescent brightener adsorbed, and, subsequently it is the method of filtering this and drying.

[0019] above 30 degrees C, particle diameter uses [the glass transition temperature of this invention] it as an organic particle 30nm or more as what has polymethacrylic acid ester, polyacrylic ester, a polyvinyl chloride, benzoguanamine resin, alkyd resin, a urea resin, a suitable vinyl chloride vinyl acetate copolymer, suitable aromatic series sulfonamide resin, etc. -- having -- as an example --; [by Nippon Paint Co., Ltd.] micro gel, a loam & Haas; acrylic emulsion,; [by Japan Synthetic Rubber Co., Ltd.] organic

particle, and Mitsui petrochemical company make --; CHEMIPEARL etc. is mentioned.
[0020] moreover, as an empty capsid, polymethacrylic acid ester, polyacrylic ester, etc. use it as a suitable thing -- having -- as an example -- the Japan Synthetic Rubber Co., Ltd. make --; empty capsid and made in loam & Haas --; empty capsid etc. is mentioned.
[0021] furthermore, above 30 degrees C, glass transition temperature uses together with the organic particle whose organic particle, part, or all 30nm or more is an empty capsid, or particle diameter As fluorescent dye used in order that these organic particles, a part, or all may obtain a fluorescence organic pigment from the organic particle which is an empty capsid The thing of any structures can be used, for example, acid dye, direct dye, cationic dye, mordant dye, acid mordant dye, a disperse dye, reactive dye, oxidation dye, etc. are used preferably. Moreover, a white fluorescent brightener is also independent or is preferably used with these fluorescent dye.
[0022] As an example of fluorescent dye ACID shown by Calah-index number - (C-I) YELLOW3, ACID YELLOW7 and ACID RED52, ACID RED77 and ACID RED87, ACID RED92 and ACID BLUE9, BACIC YELLOW1 and BACIC YELLOW40, BACIC RED1 and BACIC RED13, BACIC VIOLET7 and BACIC VIOLET10 and BACIC ORANGE22, BACIC BLUE7 and BACIC GREEN1, DISPERSEYELLOW121, DISPERSE YELLOW82, DISPERSE ORANGE11, DISPERSERED58, DISPERSE BLUE7 and DIRECT YELLOW85, DIRECT ORANGE8, DIRECT RED9, DIRECT BLUE22, DIRECT GREEN6, FLUORESCENT BRIGHTENING AGENT55 and FLUORESCENT BRIGHTENING WHITEX WS52, FLUORESCENT162, FLUORESCENT112, SOLVENT YELLOW44, SOLVENT RED49, SOLVENT BLUE5, SOLVENT PINK, SOLVENT GREEN7, PIGMENT BLUE15, PIGMENT GREEN7, PIGMENT RED53, PIGMENT RED57, PIGMENT YELLOW1 etc. is mentioned.
[0023] Moreover, as an example of a white fluorescent brightener, it is Fluoresent. Brightening Agent 85, 86, 22, 174, 166, 90, 134, 84, 24, 87, 175, 176, 169, 167, 173, 14, 32, 30, 177, 153, 168, 37, 104, 45, 55, 52, 54, 56, 171, 170, 135, 162, 163, 164, 112, 121, 172, and 91 etc. is mentioned.
[0024] When obtaining a fluorescence organic pigment, if it is desirable that it is 0.001 - 10% of the weight of within the limits and it is fewer than this, even if many [acquire / sufficient color / and / too], as for the content rate of the fluorescent dye and/or the white fluorescent brightener by which impregnation association is carried out into the organic particle an organic particle, a part, or whose all is an empty capsid, sufficient color will not be acquired to the organic particle an organic particle, a part, or whose all is an empty capsid.
[0025] Glass transition temperature moreover, the organic particle whose organic particle, part, or all 30nm or more is an empty capsid above 30 degrees C [particle

diameter] When it is used for an infrared wavelength field 700nm or more with the organic dye and/or the white fluorescent brightener which show fluorescence, glass transition temperature above 30 degrees C Particle diameter contains the organic particle whose organic particle, part, or all 30nm or more is an empty capsid. While absorbing the infrared wavelength of 700nm or more, the ink constituent which shows luminescence to an infrared region is obtained, while excelling in thermal resistance and distributed stability, a blot does not arise, but the fluorescence ink constituent excellent in lightfastness and a water resisting property is obtained.

[0026] Glass transition temperature above 30 degrees C to furthermore, the organic particle whose organic particle, part, or all 30nm or more is an empty capsid [particle diameter] If the organic dye and/or the white fluorescent brightener which show fluorescence to an infrared wavelength field 700nm or more are processed by the massive resin grinding method, the emulsion-polymerization method, the resin depositing method, etc. The organic dye and/or the white fluorescent brightener which show fluorescence to the colored infrared wavelength field which separated are incorporated in the organic particle an organic particle, a part, or whose all is an empty capsid, and impregnation association is firmly carried out. The infrared fluorescence organic pigment which maintained the property of the organic dye which shows fluorescence to an infrared wavelength field, and/or a white fluorescent brightener as it was is obtained, such an infrared fluorescence organic pigment is used and an infrared fluorescence ink constituent is obtained. Effect of the substrate at the time of printing can be made hard for the fluorescence ink constituent which used such an infrared fluorescence organic pigment to have a property as a pigment, for a blot not to produce it, even if it uses it unlike fluorescent dye, when forming a mark in paper etc., but to excel in distributed stability, lightfastness, a water resisting property, and coloring nature, to be able to give concealment nature, since it is a pigment further, and to be influenced.

[0027] As organic dye which shows fluorescence, the thing of any structures can be used for an infrared wavelength field 700nm or more, for example, poly methine system coloring matter, anthraquinone system coloring matter, dithiol metal salt system coloring matter, phthalocyanine system coloring matter, indophenol system coloring matter, aminium system coloring matter, G MONIUMU system coloring matter, azo system coloring matter, etc. are used preferably, and poly methine system coloring matter is more preferably used from a weatherproof point. Moreover, the thing same as a white fluorescent brightener as what is used for the aforementioned fluorescence ink constituent is used preferably, and may mix a colored color further.

[0028] as the example of poly methine system coloring matter -- KODAKKU

Laboratories chemical company make --;IR-140, IR[by Nippon Kayaku Co., Ltd.]-820B, etc. mention -- having -- as the example of anthraquinone system coloring matter -- the Nippon Kayaku Co., Ltd. make -- IR-750 etc. are mentioned. Moreover, as an example of dithiol metal salt system coloring matter,; tetrabuthyl HOSOHONIUMU (1, 2-benzene CHIORA-TO) NIKORE [by Mitsui Toatsu Chemicals, Inc.]-TO (III) etc. is mentioned, and Zn-naphthalocyanine etc. is mentioned as an example of phthalocyanine system coloring matter. Moreover, as an example of a white fluorescent brightener,; Mika White ACR by Nippon Kayaku Co., Ltd., Kayapor3BS, etc. are mentioned.

[0029] When obtaining an infrared fluorescence organic pigment, if it is desirable that it is 0.001 - 15% of the weight of within the limits and it is fewer than this, as for the content rate of the organic dye and/or the white fluorescent brightener which show fluorescence to the infrared wavelength field 700nm or more by which impregnation association is carried out into the organic particle an organic particle, a part, or whose all is an empty capsid, sufficient color and a fluorescence operation will not be acquired to the organic particle an organic particle, a part, or whose all is an empty capsid. Moreover, even if many [too], a color becomes deep too much, sufficient color is not acquired, concentration quenching is started and a fluorescence operation is not acquired.

[0030] Glass transition temperature thus, the organic particle whose organic particle, part, or all 30nm or more is an empty capsid above 30 degrees C [particle diameter] Use together with fluorescent dye and/or a white fluorescent brightener, or glass transition temperature above 30 degrees C Particle diameter to the organic particle whose organic particle, part, or all 30nm or more is an empty capsid The ink constituent which used the fluorescence organic pigment which carried out impregnation association of fluorescent dye and/or the white fluorescent brightener, and glass transition temperature above 30 degrees C Particle diameter the organic particle whose organic particle, part, or all 30nm or more is an empty capsid Use together with the organic dye and/or the white fluorescent brightener which have absorption in an infrared wavelength field 700nm or more, or glass transition temperature above 30 degrees C Particle diameter to the organic particle whose organic particle, part, or all 30nm or more is an empty capsid The ink constituent which used the infrared fluorescence organic pigment which made the organic particle an organic particle, a part, or whose all is an empty capsid carry out impregnation association of the organic dye and/or the white fluorescent brightener which have absorption in an infrared wavelength field 700nm or more The organic particle, the fluorescent dye and/or white fluorescent brightener, or fluorescence organic pigment these organic particle, a part, or whose all is an empty capsid, Moreover, an organic particle, a part, or all carries out

mixed distribution of the organic dye and/or white fluorescent brightener, or infrared fluorescence organic pigment which has absorption in the organic particle and the infrared wavelength field 700nm or more which are an empty capsid with a solvent, binder resin and when required, and they is prepared.

[0031] Here, each thing generally used conventionally is used as binder resin, for example, polyvinyl alcohol, acrylic resin, polyethylene oxide, starch, the formalin condensate of a naphthalene sulfonate, a carboxymethyl cellulose, etc. are used.

[0032] Moreover, as a solvent used if needed, it is independent, or they are used by water, alcohol, a ketone, ester, the ether, an aromatic hydrocarbons solvent, aliphatic hydrocarbons, etc., mixing.

[0033] Thus, the fluorescence ink constituent and infrared fluorescence ink constituent which are prepared are used for various printing methods, such as the object for ink jet printers, screen-stencil, offset printing, gravure, Toppan Printing, and an object for tampon printing, and a dispersant, a defoaming agent, a surfactant, a moisturizer, a conductive grant agent, etc. are used according to the case where it applies to various printing methods.

[0034] Especially the fluorescence ink constituent for ink jet printers and an infrared fluorescence ink constituent The relation between viscosity (mPa-s)/nozzle diameter (micrometer) is within the limits of 0.01-1. The Reynolds number within the limits of 10.5-2100 It is desirable that a Weber number has the relation between viscosity (mPa-s)/surface tension within the limits of 0.04-1.0 further within the limits of 38.2-3360. If the relation between viscosity (mPa-s)/nozzle diameter (micrometer) is within the limits of 0.03-1, a good mark can be formed, but a good mark cannot be formed if it separates from this range.

[0035] Here, it is thought that the principle which takes the lead in an ink jet print is in the electromagnetic control in formation of the drop by fission of a jet style and the flight direction of a drop. And although formation of a drop is expressed with the equation of motion of Raileigh and the hydrodynamics property of the optimal ink is acquired from the solution, it is guided as a configuration index of various kinds of dimensionless numbers also from the design condition of equipment [A.Kinoshita and the collection (1987) of printing and information record study session lecture lecture summaries]. Although there are various such dimensionless numbers, the Reynolds number and a Weber number are one of things about ink.

[0036] then, the place which examined the Reynolds number using the ink constituent of this invention -- the Reynolds number -- R=rhonul eta-1 -- [-- however, they are rho:density (g/cm3) and nu:rate-of-flow (m/s) l:nozzle diameter (micrometer) eta:coefficient of viscosity (mPa-s).] It was come out and expressed, when formation of a

drop was possible and the Reynolds number showed the range where ink flows, it needed to be within the limits of 10.5-2100, and when the ink constituent of this invention separated from the range of the above [the Reynolds number], while the satellite drop (ink drop of the diameter of a granule which is not a Maine ink drop) was formed irregularly, spilling of ink etc. arises and the target image was hard to be formed.

[0037] Moreover, when examination for choosing various nozzle diameters of an ink jet printer, printing a bar code, and deciphering the output of a bar code was performed, the image with the clearest aperture of 80 micrometers could be formed, and it became clear for printing of high power to be possible. For this reason, when the nozzle diameter was set to 80 micrometers, the rate of flow and viscosity were changed and the printing experiment was conducted, the rate of flow was able to be changed to 10 - 20 m/s, and viscosity was able to be changed to 2 - 20 mPa-s. When this is illustrated, as shown in drawing 1 , it is expressed on a curved surface, and it turns out in this case that the Reynolds numbers are 42-840.

[0038] next, the place investigated about the Weber number -- a Weber number -- W=rho nu2l.gamma-1 -- [-- however, they are rho:density (g/cm3) and nu:rate-of-flow (m/s) l:nozzle diameter (micrometer) gamma:surface tension (mN-m -1).] When it came out, and it was expressed and drop formation and foaming of ink were taken into consideration, the Weber number needed to be within the limits of 38.2-3360, and when the Weber number separated from the aforementioned range, even if the ink constituent of this invention was printable in the ability of foaming of ink not printing severely, the image formation of the object was difficult for it. Moreover, when inquired by fixing a nozzle diameter as well as the previous Reynolds number to 80 micrometers as a more desirable Weber number in the case of performing bar code printing of ranges, the rate of flow was able to change 10 - 20 m/s and surface tension to 25 - 55 mN-m -1. When this is illustrated, it is shown by the curved surface like drawing 2 , and it turns out that the Weber number in this case is changing to 152 to 1360.8.

[0039] Moreover, foaming when extruding and printing ink with an ink jet printer does not need to be uniquely decided only with surface energy, needed to take the function of viscosity and surface tension into consideration, and in the ink constituent of this invention, when the relation between viscosity (mPa-s)/surface tension (mN-m -1) was within the limits of 0.03-1.0, it was able to perform good printing. For this reason, when using the ink constituent of this invention as ink for ink jet printers, it is desirable to make it the relation between viscosity (mPa-s)/surface tension be within the limits of 0.03-1.0.

[0040] The fluorescence mark formed with such a fluorescence ink constituent and an infrared fluorescence ink constituent A light field shows fluorescence, or while

absorbing infrared light with a wavelength of 700nm or more, luminescence is shown in an infrared region. The infrared fluorescence mark which absorbs especially infrared light with a wavelength of 700nm or more, and shows luminescence to an infrared region Since there are not absorption of a visible region and luminescence, appearance of an article is not spoiled and it becomes possible [the construction material of a marked object, a configuration, etc.] to form the infrared fluorescence mark which is not further influenced by the dirt on a mark.

[0041] At the time of ** to which the reflection factor of infrared light with a wavelength of 700nm or more gives the mark which shows fluorescence to an infrared wavelength field 700nm or more to 50% or more of white marked object here It is the reflected power (standard white, made in a standard colored-paper lab: standard white No. 18) of a marked object C0 It is an output when having carried out, irradiating infrared light and measuring it to an infrared fluorescence mark, C1 If it carries out C0 / C1 a ratio is 4% or less -- desirable -- C0 / C1 when a ratio is 4% or less, it does not misoperate, even if it carries out reading actuation -- it can read and a rate can be secured.

[0042] At moreover, the time of ** to which the reflection factor of infrared light with a wavelength of 700nm or more gives an infrared fluorescence mark to 10% or less of black marked object It is an output when irradiating infrared light and measuring it to this infrared fluorescence mark, C2 If it carries out these C2 Output C1 when irradiating infrared light and measuring it to the aforementioned infrared fluorescence mark, A ratio C2 / C1 it is 5% or more -- desirable -- C2 / C1 That it is 5% or more While it can read without detecting an infrared fluorescent substance by standard Shirakami, and misoperating an infrared fluorescence mark, even if it is in a black marked lifter, an infrared fluorescence mark can be read satisfactory.

[0043] On the other hand, it is only the power ratio C0 in standard Shirakami / C1. When it considers as 4% or less, even if it can detect mark ** which shows fluorescence to an infrared wavelength field 700nm or more satisfactory, when the substrate is colored (for example, when the mark of an infrared fluorescent substance is prepared in the marked lifter containing black, especially carbon black), sufficient output cannot be obtained, but it becomes a readout error and misoperates.

[0044] Moreover, when performing the infrared fluorescence mark given to the marked lifter by high-speed reading, improvement in the speed of the speed of response from an infrared fluorescence mark is needed, but when the infrared fluorescence mark of this invention is used, 10 - 90% of build up time of the maximum output is able to carry out to less than 10microsec, and excitation light sufficient also in the time of high-speed reading of 4 or more m/s can be obtained.

[0045] Thus, while the infrared fluorescence mark formed can make hard to be

influenced effect of a blot of the dirt on a mark and ink, the effect of the substrate of a marked object can make hard to be influenced, therefore even when an infrared fluorescence mark is prepared on the marked object which has infrared absorption further, good reading can perform, and the infrared fluorescence mark which is suitable to the densification of a bar code is obtained, without limiting a marked object.

[0046] Thus, the reader which irradiates infrared light, can use it especially satisfactory as a reader which can use it for the infrared wavelength field of this invention obtained combining the mark which shows fluorescence if it is the reader which has the function in which infrared fluorescence is detectable, for example, shows drawing 3 is used.

[0047] If the reader which shows drawing 3 is explained hereafter, the reader which shows drawing 3 reads with reader optical system, it consists of circuits, and reader optical system consists of the semiconductor laser actuation circuit 1, semiconductor laser 2, a lens 3, a total reflection mirror 4, plano-convex lenses 5 and 6, a slit 7, a filter 8, and a photodiode 9.

[0048] And the excitation light 10 irradiated from said semiconductor laser 2 converges on the diameter of 1mm with a lens 3, passes along the bore 41 established in the center of a mirror 4, and is vertically irradiated to the flat surface of the infrared fluorescence mark support 11 through a lens 5. If outgoing radiation is carried out to a mirror 4 side at this time without converging the excitation light 10, since the quantity of light (excitation energy) of the excitation light 10 which a part of excitation light 10 is cut by the periphery section of said light transmission 41, therefore reaches an infrared fluorescence mark side will decrease substantially and a radiant power output will become small as a result, it is necessary to regulate the diameter of focusing for the excitation light 10 below in the diameter of said light transmission 41.

[0049] The infrared fluorescence mark 12 is conveyed in the infrared fluorescence mark support 11 top at high speed, the excitation light 10 is irradiated by this infrared fluorescence mark 12, an infrared fluorescent substance is excited, and fluorescence is received with the 1st plano-convex lens 5. It is reflected by the mirror 4, and the received light converges with the 2nd plano-convex lens 6, penetrates the slit member 7 and a filter 8, and is received with a photodiode 9.

[0050] The reading circuit consists of an amplifying circuit, the detector 13 equipped with the filter circuit, the binarization processing circuit 14, a decoding circuit 15, a serial interface 16, and a personal computer 17 for data processing.

[0051]

[Example] Next, the example of this invention is explained. In addition, it cannot be overemphasized that this invention is not what is limited to these examples.

To the empty capsid dispersion-liquid (20 % of the weight [of solid content], particle

diameter [of 0.3 microns], glass transition temperature of 30 degrees C) 100 weight section of example 1 styrene acrylic ester system resin, the solution which dissolved the Rhodamine B (Sumitomo Chemical Co., Ltd. make) 0.3 weight section in the ethanol 6 weight section was added, it stirred and mixed and the peach-colored fluorescence organic pigment was obtained. To this, after carrying out 20 weight sections addition of 10 weight sections and the water and carrying out mixed distribution of the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) with a ball mill for 3 hours, the ink constituent was prepared through the 1-micron filter. For the Reynolds number of this ink constituent, 560 and a Weber number were [0.0375, and the viscosity/surface tension of 1018, and viscosity/nozzle diameter] 0.09. And it printed in the paper with the ink jet printer using the ink constituent obtained by doing in this way.

[0052] To the emulsion-polymerization solution (30 % of the weight [of solid content], particle diameter [of 50nm], glass transition temperature of 50 degrees C) 100 weight section of example 2 styrene acrylic ester system resin, the solution which dissolved the Rhodamine B (Sumitomo Chemical Co., Ltd. make) 0.3 weight section in the ethanol 6 weight section was added, it stirred and mixed and the peach-colored fluorescence organic pigment was obtained. To this, after carrying out 20 weight sections addition of 10 weight sections and the water and carrying out mixed distribution of the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) with a ball mill for 3 hours, the ink constituent was prepared through the 1-micron filter. For the Reynolds number of this ink constituent, 400 and a Weber number were [0.05, and the viscosity/surface tension of 842, and viscosity/nozzle diameter] 0.1. And it printed in the paper with the ink jet printer using the ink constituent obtained by doing in this way.

[0053] To the emulsion-polymerization solution (30 % of the weight [of solid content], particle diameter [of 50nm], glass transition temperature of 50 degrees C) 100 weight section of example 3 styrene acrylic ester system resin, the solution which dissolved the ASUTORAZON red 6B(Bayer make) 0.2 weight section in the ethanol 4 weight section was added, it stirred and mixed and the peach-colored fluorescence organic pigment was obtained. To this, after carrying out 20 weight sections addition of 10 weight sections and the water and carrying out mixed distribution of the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) with a ball mill for 3 hours, the ink constituent was prepared through the 1-micron filter. For the Reynolds number of this ink constituent, 315 and a Weber number were [0.05, and the viscosity/surface tension of 473, and viscosity/nozzle diameter] 0.1. And it printed in the paper with the ink jet printer using the ink constituent obtained by doing in this way.

[0054] To the emulsion-polymerization solution (30 % of the weight [of solid content], particle diameter [of 50nm], glass transition temperature of 50 degrees C) 100 weight section of example 4 styrene acrylic ester system resin, the solution which dissolved the solar pure yellow 8G (Sumitomo Chemical Co., Ltd. make) 0.2 weight section in the ethanol 4 weight section was added, it stirred and mixed and the peach-colored fluorescence organic pigment was obtained. To this, after carrying out 20 weight sections addition of 10 weight sections and the water and carrying out mixed distribution of the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) with a ball mill for 3 hours, the ink constituent was prepared through the 1-micron filter. For the Reynolds number of this ink constituent, 236 and a Weber number were [0.067, and the viscosity/surface tension of 405, and viscosity/nozzle diameter] 0.11. And it printed in the paper with the ink jet printer using the ink constituent obtained by doing in this way.

[0055] It added stirring the solution made to dissolve the IR-820 (Nippon Kayaku Co., Ltd. make; peak:820nm [of poly methine system coloring matter and absorption wavelength], peak:900nm of luminescence wavelength) 0.15 weight section in the acetone 5 weight section to the emulsion-polymerization solution (30 % of the weight [of solid content], particle diameter [of 30nm], glass transition temperature of 40 degrees C) 100 weight section of example 5 styrene acrylic ester system resin, and the infrared fluorescence organic pigment was obtained. To this, 10 weight sections addition of 10 weight sections and the water was carried out, the ball mill distributed the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) for 3 hours, and the ink constituent was prepared to it. For the Reynolds number of this ink constituent, 475 and a Weber number were [0.0438, and the viscosity/surface tension of 1008, and viscosity/nozzle diameter] 0.11. Thus, bar code printing was carried out at one Japanese paper which divided the obtained ink constituent into the portion and 5% of portion whose reflection factor of 800nm infrared light is 70% using the ink jet printer.

[0056] The solution made to dissolve the IR-140 (made in KODAKKU Laboratories Chemicals; peak:826nm [of poly methine system coloring matter and absorption wavelength], peak:870nm of luminescence wavelength) 0.1 weight section in the dimethyl sulfoxide 5 weight section was added to the emulsion-polymerization solution (30 % of the weight [of solid content], particle diameter [of 40nm], glass transition temperature of 40 degrees C) 100 weight section of example 6 styrene acrylic ester system resin, stirring, and the infrared fluorescence organic pigment was obtained. To this, 10 weight sections addition of 10 weight sections and the water was carried out, the ball mill distributed the JON krill 61 (Johnson polymer company make; acrylic

styrene resin, 30 % of the weight of solid content) for 3 hours, and the ink constituent was prepared to it. For the Reynolds number of this ink constituent, 216.3 and a Weber number were [0.0714, and the viscosity/surface tension of 463.5, and viscosity/nozzle diameter] 0.14. Thus, bar code printing was carried out at one Japanese paper which divided the obtained ink constituent into the portion and 3% of portion whose reflection factor of 800nm infrared light is 60% using the ink jet printer.

[0057] It added stirring the solution made to dissolve the IR-820 (Nippon Kayaku Co., Ltd. make; peak:820nm [of poly methine system coloring matter and absorption wavelength], peak:900nm of luminescence wavelength) 0.15 weight section in the acetone 5 weight section to the emulsion-polymerization solution (30 % of the weight [of solid content], particle diameter [of 30nm], glass transition temperature of 40 degrees C) 100 weight section of example 7 styrene acrylic ester system resin, and the infrared fluorescence organic pigment was obtained. To this, 10 weight sections addition of 10 weight sections and the water was carried out, the ball mill distributed the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) for 3 hours, and the ink constituent was prepared to it. For the Reynolds number of this ink constituent, 288 and a Weber number were [0.0714, and the viscosity/surface tension of 721, and viscosity/nozzle diameter] 0.13. Thus, bar code printing was carried out at one Japanese paper which divided the obtained ink constituent into the portion and 5% of portion whose reflection factor of 800nm infrared light is 70% using the ink jet printer.

[0058] It added stirring the solution which dissolved the Rhodamine B (Sumitomo Chemical Co., Ltd. make) 0.15 weight section in the acetone 4 weight section to the emulsion-polymerization solution 100 weight section of the organic particle (20 % of the weight of solid content, particle diameter of 20nm, glass transition temperature of 40 degrees C) of example of comparison 1 styrene acrylic ester system resin, and the red fluorescence organic pigment was obtained. To this, after adding the water 20 weight section and carrying out mixed distribution with a ball mill for 3 hours, the ink constituent was prepared through the 1-micron filter. And it printed in the paper with the ink jet printer using the ink constituent obtained by doing in this way.

[0059] It added stirring the solution which dissolved the ASUTORAZON red 6B(Bayer make) 0.3 weight section in the acetone 6 weight section to the emulsion-polymerization solution (30 % of the weight [of solid content], particle diameter [of 3 microns], glass transition temperature of 30 degrees C or less) 100 weight section of example of comparison 2 butyl acrylate, and the yellow fluorescence organic pigment was obtained. To this, after adding the water 20 weight section and carrying out mixed distribution with a ball mill for 3 hours, the ink constituent was prepared through the 5-micron filter.

And it printed in the paper with the ink jet printer using the ink constituent obtained by doing in this way.

[0060] Stirring mixing of the example of comparison 3 Rhodamine B (Sumitomo Chemical Co., Ltd. make) 2 weight section, the water 80 weight section, the glycerol 15 weight section, and the ethylene glycol 15 weight section was carried out, and the ink constituent was prepared through the 1-micron filter. And it printed in the paper with the ink jet printer using the ink constituent obtained by doing in this way.

[0061] It added mixing the solution made to dissolve the example of comparison 4IR820B(Nippon Kayaku Co., Ltd. make; peak:820nm [of poly methine system coloring matter and absorption wavelength], peak:900nm of luminescence wavelength) 0.15 weight section in the acetone 2 weight section in the solution which mixed the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) 30 weight section, and the water 90 weight section, and the ink constituent was prepared. Thus, bar code printing was carried out at one Japanese paper which divided the obtained ink constituent into the portion and 5% of portion whose reflection factor of 800nm infrared light is 70% using the ink jet printer.

[0062] It added mixing the solution made to dissolve the example of comparison 5IR140 (made in KODAKKU Laboratories Chemicals; peak:826nm [of poly methine system coloring matter and absorption wavelength], peak:870nm of luminescence wavelength) 0.05 weight section in the dimethyl sulfoxide 5 weight section in the solution which mixed the JON krill 61 (Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) 30 weight section, and the water 90 weight section, and the ink constituent was prepared. Thus, bar code printing was carried out at one Japanese paper which divided the obtained ink constituent into the portion and 3% of portion whose reflection factor of 800nm infrared light is 60% using the ink jet printer.

[0063] The ball mill distributed the example of comparison 6 inorganic fluorescent substance LiNd0.5 Yb0.5 P4 O128 weight section, the JON krill 61(Johnson polymer company make; acrylic styrene resin, 30 % of the weight of solid content) 6 weight section, and the water 40 weight section, and the ink constituent was prepared. Thus, bar code printing was carried out at one Japanese paper which divided the obtained ink constituent into the portion and 5% of portion whose reflection factor of 800nm infrared light is 70% using the ink jet printer.

[0064] About the ink constituent and print which were obtained in examples 1-4 and the examples 1-3 of a comparison, storage stability, lightfastness, blot nature, remelting nature, and an imprint property were examined by the following method. In addition, in this example and the example of a comparison, using ink jet printer [by Hitachi, Ltd.];GX-PA (nozzle diameter: 80 micrometers) as an ink jet printer, it prints, and using

the differential scanning calorimeter made from Perkin-Elmer (DSC-7), temperature up of the sample which carried out the desiccation solidification of the solution of an organic particle at 80 degrees C for 24 hours is carried out, and the glass transition temperature of an organic particle measures it by -20 degrees C to 5 degrees C / min.

[0065] <Storage stability> each ink constituent was saved in the 50-degree C thermostat for 100 hours, sedimentation of a fluorescent pigment was investigated, and the case where there were (O) and sedimentation about the case where there is no sedimentation was evaluated as (x).

[0066] <Light-fast> each print was irradiated in fade meter for 5 hours, discoloration was observed visually, and the case where there were (O) and discoloration about a thing without discoloration was evaluated as (x).

[0067] The blot of the printing side of <blot nature> each print was observed, and the case where there were (O) and a blot about the case where there is no blot was evaluated as (x).

[0068] <Remelting nature> each ink constituent is dropped on a PET film, desiccation solidification was carried out in the greenhouse for 24 hours, the alkaline water of pH11 was dropped at this, and (O) and the thing which is not re-distributed were evaluated for what is re-distributed as (x).

[0069] Applied the 5kg load to a 20-sheet pile and this, saved at the 30-degree C thermostat for 600 hours, what does not imprint <imprint property> each print was made into (O), and what is imprinted was made into (x). As a result, the following table 1 is.

[0070]

表1

	貯蔵安定性	耐候性	滲み性	再溶解性	転写特性
実施例1	○	○	○	○	○
〃 2	○	○	○	○	○
〃 3	○	○	○	○	○
〃 4	○	○	○	○	○
比較例1	○	○	×	×	○
〃 2	×	○	○	○	×
〃 3	○	×	×	○	○

[0071] Moreover, the emission spectrum of the printing side of the print obtained in examples 5 and 6 and the examples 4 and 5 of a comparison was measured using the UNISOKU spectrum measuring device. Drawing 4 and drawing 5 show the result, drawing 4 shows the emission spectrum of the printing side of the print obtained in the example 5 and the example 4 of a comparison, and drawing 5 shows the emission spectrum of the printing side of the print obtained in the example 6 and the example 5 of a comparison. Although it has shifted to dozens of nm long wavelength side from the infrared fluorescent dye used as a raw material so that clearly from this drawing 4 and drawing 5 , it turns out that the property of the infrared fluorescent dye of a basis is held.

[0072] Next, it measured on condition that the high-speed readout of 4 m/s with the detector which shows the reflected power of a substrate, and the output of the infrared fluorescence mark of a bar code to drawing 3 about bar code printing of the Japanese paper obtained in examples 5-7 and the examples 4-6 of a comparison. It sets to this measurement and is the reflected power in the place of 50% of reflection factors C0 It carries out and is the output of the infrared fluorescence mark in the place of 50% of reflection factors C1 C0 when carrying out and setting the output of the infrared fluorescence mark of the portion of 10% of reflection factors to C2 C1 A ratio and C2 C1 The ratio was measured. Moreover, the readout of each bar code was performed about 100 samples, and (O) and less than 95% of case were evaluated for the case where the rate of a readout is 95% or more, as (x). Furthermore, the printing object was observed visually and (x) and the case where it was not blurred were evaluated for the case where it is blurred, as (O). As a result, the following table 2 is.

[0073]

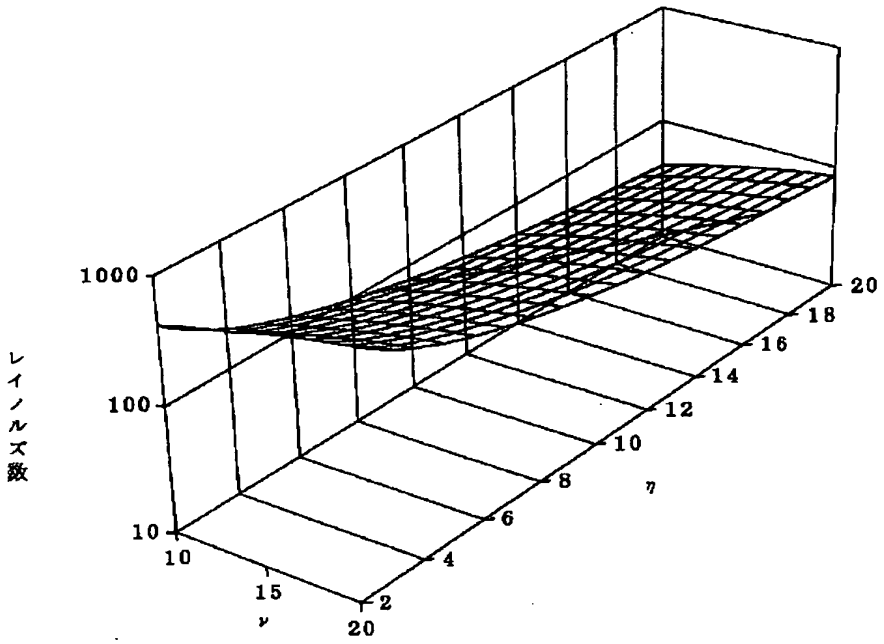
表2

	滲み	C_0 ／C_1 (%)	C_2 ／C_1 (%)	読み取り
実施例5	○	2.5	15	○
〃 6	○	2.5	10	○
〃 7	○	2.8	9	○
比較例4	×	2.4	0	×
〃 5	×	2.6	0	×
〃 6	○	2	10	×

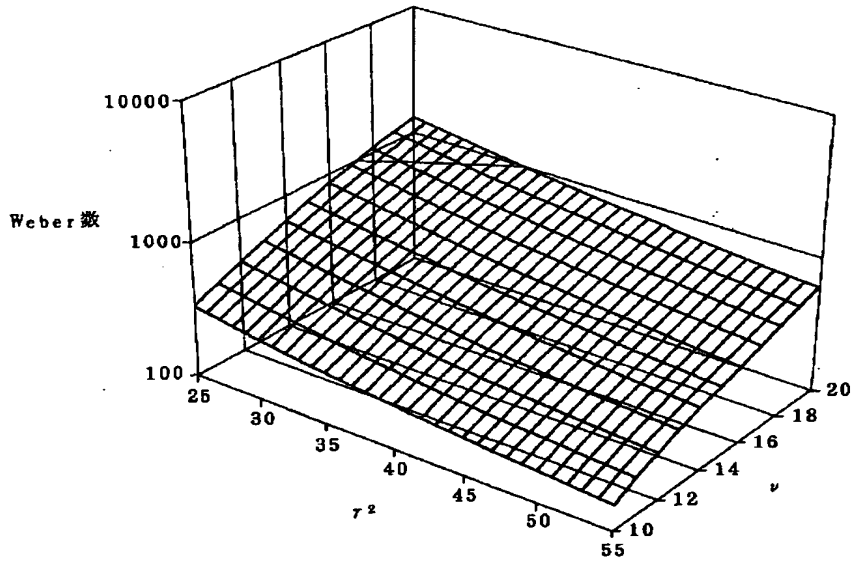
[0074]
[Effect of the Invention] The ink constituent which used the fluorescence organic pigment obtained in the examples 1-4 so that clearly from the above-mentioned table 1 What was printed with the ink constituent which used the fluorescence organic pigment from which distributed stability was good and was acquired in the examples 1-4 All are compared with what was printed and printed with the ink constituent which used the fluorescent dye of the examples 1-3 of a comparison, there is no blot, lightfastness and a water resisting property are good, and it turns out that according to this invention there is no blot and the fluorescence ink constituent distributed stability, lightfastness, and a deck watertight luminaire excelled [constituent] in the sex is obtained.
[0075] Moreover, the infrared fluorescence mark (an example 5 thru/or 7) which consists of a bar code printed by Japanese paper by this invention so that clearly from the above-mentioned table 2 The infrared fluorescence mark compare with the infrared fluorescence mark (examples 4 and 5 of a comparison) which consists of a bar code printed by conventional Japanese paper, there is no blot, and the rate of reading is good, and according to this invention from this It is hard to be influenced of a blot by the dirt on a mark, or ink, and it is hard to be influenced of the substrate of a marked object, and it turns out that it is the stable high-concentration infrared fluorescence mark which does not choose a marked object.
[0076] Furthermore, the infrared fluorescence mark (an example 5 thru/or 7) which consists of a bar code printed by Japanese paper by this invention is understood that good reading is possible, without comparing with the infrared fluorescence mark which consists of an inorganic fluorescent substance of the example 6 of a comparison, and causing an operation mistake also in high-speed reading.

[Brief Description of the Drawings]
[Drawing 1] It is analysis drawing of the Reynolds number of the fluorescence ink constituent of this invention.
[Drawing 2] It is analysis drawing of the Weber number of the fluorescence ink constituents of this invention.
[Drawing 3] It is approximate account drawing showing an example of the reader which detects infrared fluorescence.
[Drawing 4] It is the emission spectrum of the printing side of the print obtained in the example 5 and the example 4 of a comparison.
[Drawing 5] It is the emission spectrum of the printing side of the print obtained in the example 6 and the example 5 of a comparison.

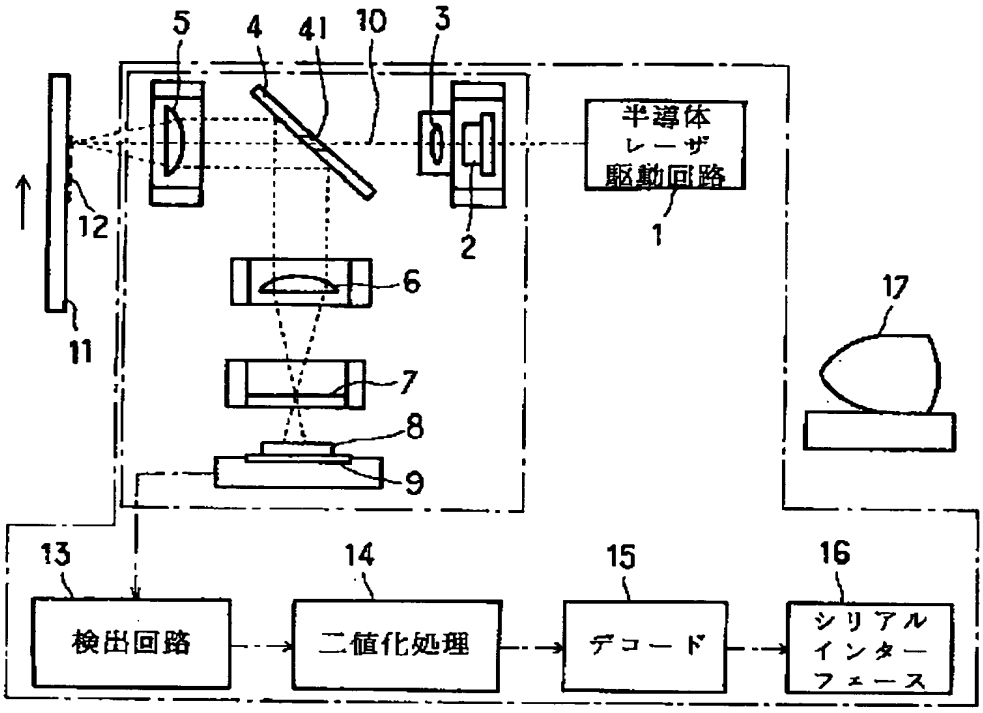
[Drawing 1]



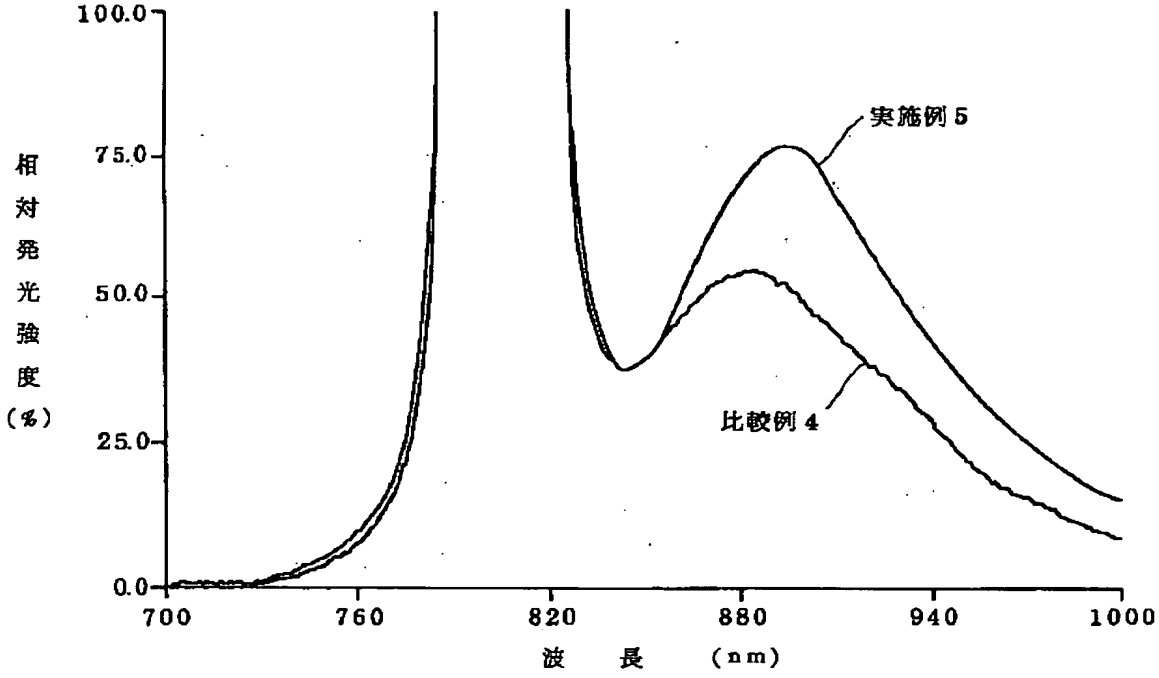
[Drawing 2]



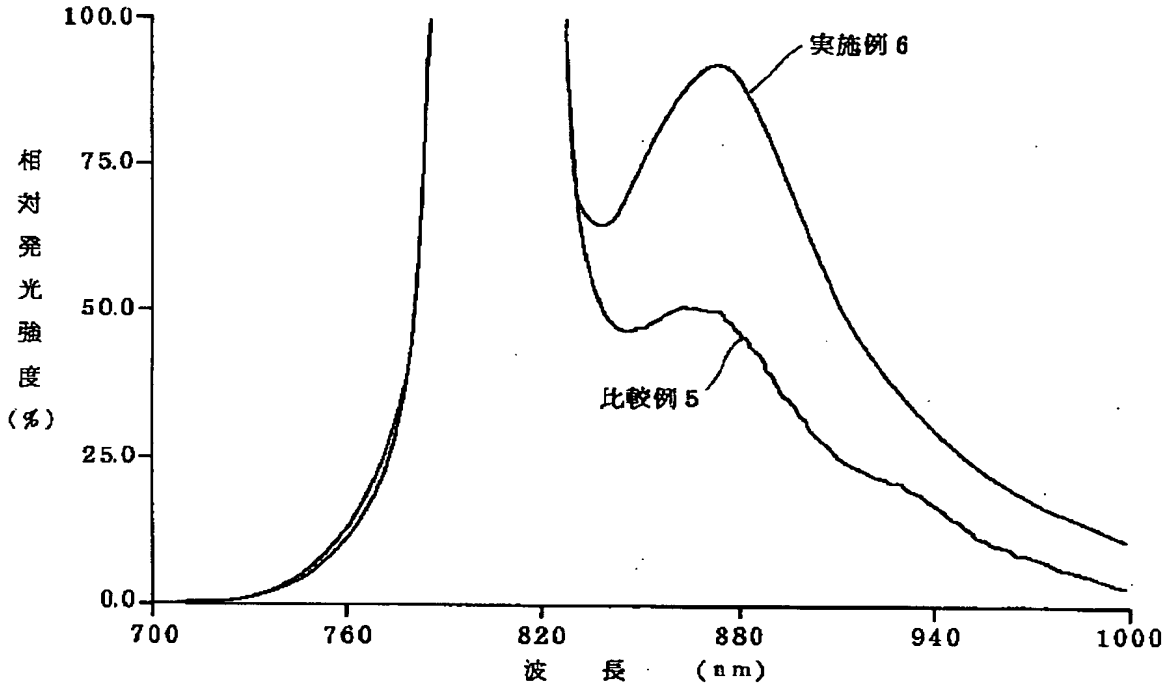
[Drawing 3]



[Drawing 4]



[Drawing 5]


100.0
75.0
50.0
25.0
0.0
相対発光強度（%）
700
760
820
880
940
1000
波長（nm）
実施例 6
比較例 5